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Short communication

Enhancement of thermal stability and cycling performance in lithium-ion cells through the use of ceramic-coated separators

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ABSTRACT

Ceramic-coated separators are prepared by coating the sides of a porous polyethylene membrane with nano-sized Al_2O_3 powder and hydrophilic poly(lithium 4-styrenesulfonate) binder. These separators exhibit an improved thermal stability at high temperatures without significant thermal shrinkage. Due to the high hydrophilicity of the polymer binder and large surface area of the small ceramic particles, the separators show good wettability in non-aqueous liquid electrolytes. By using the ceramic-coated separators, lithium-ion cells composed of a carbon anode and a $LiCoO_2$ cathode are assembled and their cycling performance is evaluated. The cells are proven to have better capacity retention than for cells prepared with polyethylene membrane. It is expected that the ceramic-coated separator in this study can be potential candidate as a separator for rechargeable lithium-ion batteries that require thermal safety and good capacity retention.

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1. Introduction

Lithium-ion batteries have rapidly dominated the power-source market for portable electronic devices, power tools, and electric vehicles due to their high energy density and excellent cycle life. For lithium-ion batteries, a separator is a critical component that prevents physical contact of the positive and negative electrodes while permitting free ionic transport within the cell. Proper selection of the separator is very important for achieving good battery performance with respect to cycle life, energy density, power density, and safety [1]. Most of the separators currently used in lithium-ion batteries are based on microporous polyolefin membranes, including polyethylene and polypropylene, as well as various combinations of the two [2,3]. Although such membranes offer excellent mechanical strength and chemical stability, they exhibit large thermal shrinkage at high temperatures [4–6], which causes a short circuit between electrodes in cases of unusual heat generation. In order to solve this problem, inorganic composite separators have been developed by combining the characteristics of polymeric nonwoven and ceramic materials [7–9]. Separators should be also wet in the electrolyte and permanently retain the electrolyte solution; however, the large difference in polarity between the non-polar polyolefin separator and the highly polar organic electrolyte leads to poor wettability. As a result of this poor wettability, there is a high resistance when the pores in the separator are not completely filled with the liquid electrolyte [10]. Therefore, separators with enhanced thermal stability and good wettability in organic liquid electrolytes are highly desirable for the development of lithium-ion batteries with enhanced safety and good cycling performance.

In the present study, we tried to improve the thermal stability and wettability of a microporous polyethylene (PE) membrane by coating both sides of the membrane with nano-sized ceramic powders and a hydrophilic polymer binder. Due to the presence of a heat-resistant ceramic powder with a high surface area and a hydrophilic polymer binder, the ceramic-coated separator exhibited good thermal stability and wettability in non-aqueous liquid electrolytes. Using these ceramic-coated separators, we assembled lithium-ion cells composed of a carbon anode and a $LiCoO_2$ cathode, and their cycling performances were evaluated.

2. Experimental

2.1. Preparation of the ceramic-coated separator

Ceramic-coated separators were prepared from nano-sized ceramic powder and a hydrophilic polymer binder. Poly(lithium 4-styrenesulfonate) (PLSS, Aldrich Chem. Co.) and aluminum oxide (Al_2O_3) powder with a particle size of 2–4 nm (Aldrich Chem. Co.) were used as the raw materials for making the ceramic-coated separators. These materials were put into a water/*N*,*N*-dimethylacetamide solvent mixture (5/95, v/v), and uniformly dispersed by ball milling overnight. The resulting slurry

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Table 1
Composition and thickness of the ceramic-coated separators.

Thickness (μm)	Al_2O_3: PLSS (w/w ratio)	Sample designation
25	None	PE
28	1:1	ACS[a]-1
	1:2	ACS-2
30	1:1	ACS-3
	1:2	ACS-4

[a] Alumina-coated separator.

was then coated onto both sides of a microporous PE membrane substrate with a thickness of 25 μm and a porosity of 40%. Next, the separator was dried at room temperature for 10 min to allow the solvent to evaporate, followed by additional drying in a vacuum oven at 80 °C for more than 24 h. The thickness of the ceramic-coated separator was controlled by changing the content of polymer binder and ceramic powder in the slurry. The total thickness of the ceramic-coated separator was kept at less than 30 μm in order to avoid losing the high energy density, which is one of the most important advantages of lithium-ion batteries. The weight ratios of Al_2O_3 powder and polymer binder that were coated onto the PE substrate, as well as the resulting thicknesses of the respective ceramic-coated separators, are given in Table 1.

2.2. Electrode preparation and cell assembly

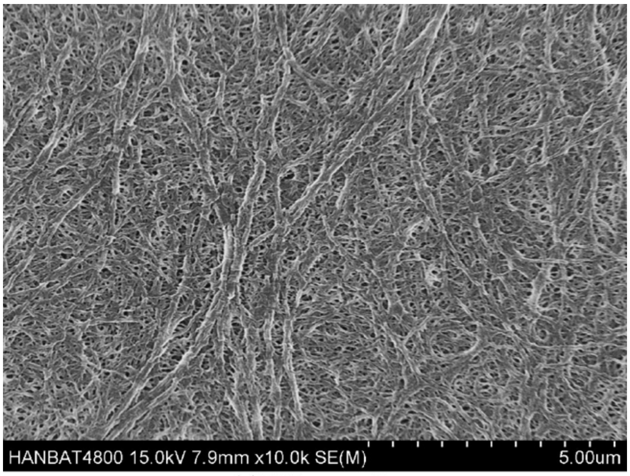
The cathode was prepared by coating the *N*-methyl pyrrolidine (NMP)-based slurry containing $LiCoO_2$ (Japan Chemical), poly(vinylidene fluoride) (PVdF), and super-P carbon (MMM Co.) on an aluminum foil. The carbon anode was prepared similarly by coating the NMP-based slurry of mesocarbon microbeads (MCMB, Osaka gas), PVdF, and super-P carbon on a copper foil. The thicknesses of the electrodes ranged from 50 to 60 μm after roll pressing, and their active mass loading corresponded to a capacity of about 2.84 mAh cm^{-2}. Lithium-ion cells were assembled by sandwiching the ceramic-coated separator between the carbon anode and the $LiCoO_2$ cathode. The cell was then enclosed in a pouch bag and injected with the same amount of electrolyte solution, which consisted of 1.0 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v, Techno Semichem Co., Ltd.). All cells were assembled in a dry box filled with argon gas.

2.3. Measurements

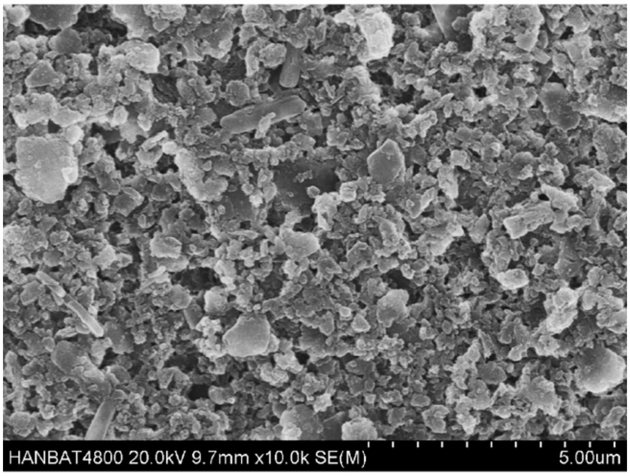
The surface morphologies of the PE membranes and ceramic-coated separators were examined using a scanning electron microscope (JEOL, JSM-6300). Thermal shrinkage of the ceramic-coated separators in the form of dimensional change was measured before and after being kept at 105 °C for 1 h. In order to measure electrolyte uptake and ionic conductivity, the ceramic-coated separator was immersed in 1.0 M $LiPF_6$ in EC/DMC for 1 h. Afterward, the separator was taken out from the electrolyte solution and excess electrolyte solution on the surface of separator was removed by wiping with filter paper. The uptake of electrolyte solution was determined using the following relationship:

$$\text{uptake}\,(\%) = \frac{W - W_o}{W_o} \times 100$$

Here, W_o and W are the weights of the separator before and after soaking in the liquid electrolyte, respectively. The wetted separator was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. AC impedance measurements were performed to measure ionic conductivity using an impedance analyzer over the frequency range of 10 Hz to 100 kHz with an amplitude of 10 mV. Charge and discharge cycling tests of the lithium-ion cells were conducted at a current density of 1.42 mA cm^{-2} (0.5 C rate) over a voltage range of 2.8–4.2 V with battery test equipment.



(a) PE separator



(b) Ceramic-coated separator

Fig. 1. Scanning electron micrographs of the surface of a porous PE membrane and ceramic-coated separator (ACS-3).

3. Results and discussion

Scanning electron micrographs of the surface of the porous PE membrane and the ceramic-coated separator (ACS-3) are presented in Fig. 1. The PE membrane exhibited a uniformly interconnected submicron pore structure. As the Al_2O_3 powder with polymer binder was coated onto the PE substrate, the ceramic particles were covered the polymer binder, due to the high volumetric ratio of polymer binder to ceramic powder. We also observed the formation of large pores in the coating layer of the ceramic-coated separator, the presence of which was expected to lead to efficient uptake of the liquid electrolyte upon immersion in an electrolyte solution.

The uptake of an electrolyte solution in the ceramic-coated separator and the ionic conductivity after soaking in the liquid electrolyte (1.0 M $LiPF_6$–EC/DMC) were measured and are summarized in Table 2. Ionic conductivity of liquid electrolyte used in soaking the separators is 1.1×10^{-2} S cm^{-1} at room temperature. For comparison purposes, a microporous PE membrane was soaked in the same electrolyte solution, and the resulting experimental data is included in Table 2. As expected, the non-polar PE membrane exhibited poor wettability and electrolyte retention

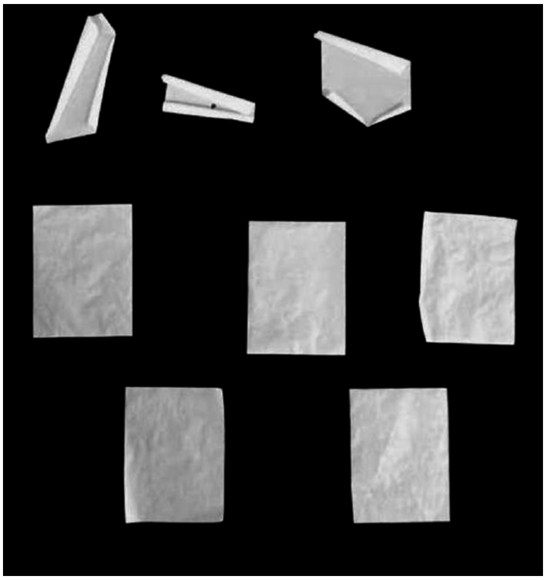


Fig. 2. Photographs of PE membranes and ceramic-coated separators (ACS-3) after being kept at 105 °C for 1 h.

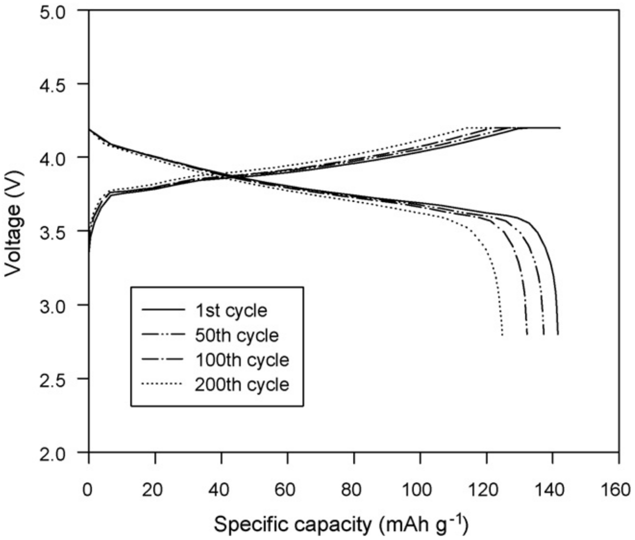


Fig. 3. Charge and discharge curves of lithium-ion cell assembled with the ceramic-coated separators (ACS-3) (0.5 C CC and CV charge, 0.5 C CC discharge, cut-off: 2.8–4.2 V).

due to its inherent hydrophobic properties. For the ceramic-coated separators, the amount of electrolyte absorbed was greater than the amount absorbed by the PE membrane, which resulted in higher ionic conductivity. This result was due to the high hydrophilicity of the polymer binder and the high surface area of the nano-sized Al_2O_3 particles. In addition, since the poly(lithium 4-styrenesulfonate) had a large number of lithium ions in the side chains and had a high affinity for the electrolyte solution, a higher amount of electrolyte solution was expected to be retained by the separator. Indeed, the wettability and ionic conductivity of the ceramic-coated separator were found to increase slightly with increasing thickness of the coating layer and the relative composition of polymer binder to Al_2O_3 particles. Ionic conductivity of PE separator filled with electrolyte solution is lower than that of electrolyte solution, which is due to the fact that the specific resistivity of the separator saturated with liquid electrolyte is increased by the combination of tortuosity and porosity of the separator [3]. Ionic conductivities of the ceramic-coated separators after soaking in the electrolyte solution ranged from 7.2×10^{-4} to 8.3×10^{-4} S cm^{-1} at room temperature.

In order to evaluate the heat-resistant properties of the ceramic-coated separators, we measured thermal shrinkage after storing the separators at 105 °C for 1 h (Table 2). Photographs of the PE membranes and the ceramic-coated separators (ACS-3) after being kept at 105 °C for 1 h are shown in the top and bottom of Fig. 2, respectively. The photographs clearly show that the PE membranes underwent a high degree of shrinkage (13.8%) during exposure to the high temperature conditions. Since the manufacturing process of microporous PE membranes includes a drawing step, membranes shrinks easily when exposed to high temperature, due to internal stress [1]. Consequently, PE membranes would lose mechanical stability upon exposure to high temperatures, which may result in physical contact between the anode and the cathode. On the other hand, thermal shrinkage was significantly reduced by coating both sides of the PE membrane with Al_2O_3 powder and polymer binder. It is considered that coating heat-resistant ceramic particles onto both sides of the porous PE membrane can prevent dimensional changes by thermal deformation because of the frame structure of the heat-resistant ceramic powder with polymer binder. The lowest degree of shrinkage was obtained with ACS-3, suggesting that thermal stability of a PE membrane can indeed be enhanced by increasing either the content of the ceramic particles or the thickness of the coating layer.

We evaluated the cycling performance of lithium-ion cells prepared with the ceramic-coated separator. Assembled cells were initially subjected to a preconditioning cycle in the voltage range of 2.8–4.2 V at constant current rates of 0.05, 0.1 and 0.2 C, consecutively. After three cycles, cells were charged at a current density of 1.42 mA cm^{-2} (0.5 C rate) up to a target voltage of 4.2 V. This was followed by a constant voltage charge with a decline of current until a final current was reached to 20% of the charging current. The cells were then discharged to a cut-off voltage of 2.8 V at the same current density (0.5 C rate). Fig. 3 shows the charge–discharge curves of the 1st, 50th, 100th and 200th cycles of the lithium-ion cell assembled with the ceramic-coated separator (ACS-3). The cell had an initial discharge capacity of 141.6 mAh g^{-1} based on active $LiCoO_2$ material in the cathode. The discharge capacity of the cell declined to 124.8 mAh g^{-1} after 200 charge/discharge cycles, which corresponded to 88.1% of the initial discharge capacity. The coulombic efficiency of the cell increased steadily and stabilized with cycle number and was maintained at greater than 99.0% after the initial few cycles.

Fig. 4 shows the discharge capacities of lithium-ion cells assembled with different separators as a function of cycle number. The cycling characteristics of the cells were found to depend on the

Table 2
Electrolyte uptakes, ionic conductivities, and thermal shrinkage of the ceramic-coated separators.

Separator	Electrolyte uptake (%)	Ionic conductivity (S cm^{-1})	Thermal shrinkage (%)
PE	116.5	2.5×10^{-4}	13.8
ACS-1	206.7	7.2×10^{-4}	6.1
ACS-2	237.8	8.1×10^{-4}	7.6
ACS-3	218.5	7.6×10^{-4}	3.8
ACS-4	248.4	8.3×10^{-4}	4.5

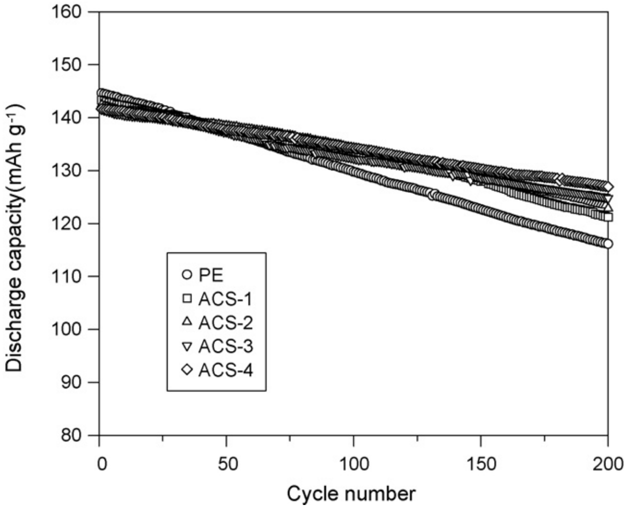


Fig. 4. Discharge capacities of the lithium-ion cells prepared with a PE membrane and ceramic-coated separators (0.5 C CC and CV charge, 0.5 V CC discharge, cut-off: 2.8–4.2 V).

type of separator. The initial discharge capacity of the cell was slightly decreased by coating the PE membrane with Al_2O_3 powder and polymer binder. Presence of an additional coating layer on the porous PE membrane may have increased the resistance of ion migration in the separator, giving rise to a reduced discharge capacity; however, the capacity retention was improved by coating Al_2O_3 powder and polymer binder onto the porous PE membrane. It was thought that the ability to retain electrolyte solution in the pores of the ceramic-coated separator was higher than in the hydrophobic PE membrane alone, and thus helped to prevent a lack or leak of electrolyte during repeated cycling. When examining the effect of the ratio of Al_2O_3 powder and polymer binder on the cell performance, the cell assembled with ceramic-coated separator containing high content of polymer (PLSS) exhibited better capacity retention.

The rate capability of the lithium-ion cell prepared with the ceramic-coated separator was evaluated. Cells were charged to 4.2 V at a constant current of 0.2 C and discharged at different current rates ranging from 0.1 to 2.0 C. The discharge curves of the lithium-ion cell assembled with ACS-2 are given in Fig. 5. Both the voltage and the capacity decreased gradually with increasing rates of current. Fig. 6 compares the relative discharge capacities of lithium-ion cells prepared with different separators as a function of current density, where relative capacity was defined as the ratio of the discharge capacity at a specific C rate to the discharge delivered at a rate of 0.1 C. The results showed that the coating layer thickness affected high rate performance. The high rates of performance of the cells assembled with ACS-1 or ACS-2 could be ascribed to favorable interfacial charge transport between the electrodes and the electrolytes in the cell, because the coating layer on both sides of the PE membrane was able to assist in adhering the separator to the electrodes after soaking in the electrolyte solution. In the case of ACS-3 or ACS-4, the thick coating layer on the porous PE membrane may have hampered the ion migration in the separator even if the coating layer on the PE membrane improved interfacial adhesion, the result of which was a decreased discharge capacity at high current rates.

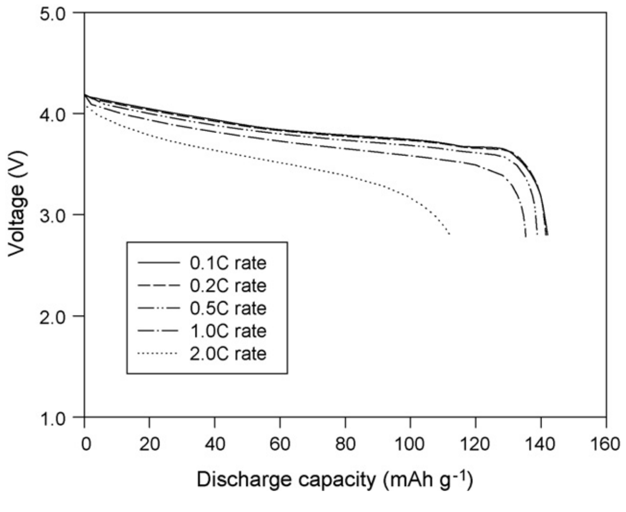


Fig. 5. Discharge profiles of lithium-ion cell prepared with ceramic-coated separator (ACS-2) as function of C rate. The charge rate was 0.2 C with a 4.2 V cut-off.

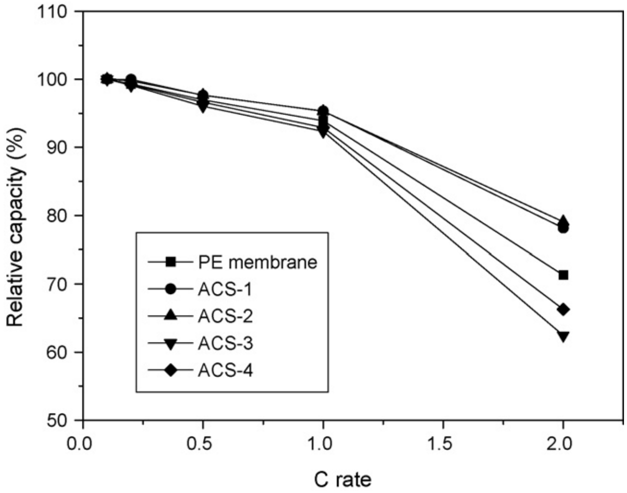


Fig. 6. Relative capacities of lithium-ion cells prepared with PE membrane or ceramic-coated separators as a function of C rate.

4. Conclusions

Ceramic-coated separators were prepared by coating nano-sized Al_2O_3 powder and hydrophilic poly(lithium 4-styrenesulfonate) onto both sides of a porous PE membrane. These separators exhibited enhanced thermal stability by retaining stable dimensions at high temperatures. Due to the high hydrophilicity of the polymer binder and high surface area of the small inorganic particles, the coated membranes exhibited good wettability in non-aqueous liquid electrolytes. As a result, the lithium-ion cells assembled with the ceramic-coated separators exhibited better capacity retention than did the cells prepared with only a PE membrane. It is expected that the ceramic-coated separators described in this study may be useful as separators for rechargeable lithium-ion batteries that require thermal safety and good capacity retention.

Acknowledgements

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